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IONIZATION ENHANCED MIGRATION OF RADIATION PRODUCED DEFECTS IN SILICON

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Abstract

Evidence for ionization enhanced migration of radiation produced defects in silicon is reviewed. Detailed results from EPR and DLTS studies are presented for the lattice vacancy, interstitial boron, and interstitial aluminum. The implications of these results to the mystery of the low temperature migration of interstitial silicon are discussed.

I. Introduction

The phenomenon of ionization enhanced diffusion of defects in semiconductors is well documented. In fact, one of the first reported examples was in silicon by Gregory[1] where it was shown that an annealing stage at ∿160°K attributed to long range migration of the vacancy in p-type material could be induced by electrical injection of minority carriers at 77K. More recently, dramatic examples have been found in GaP and GaAs where several specific defects produced by irradiation and normally stable at room temperature, can be annealed rapidly under minority carrier injection conditions.[2-5] This phenomenon is believed to be of practical importance and concern in compound semiconductor devices which often degrade under operating injection conditions.[6]

The mechanisms for ionization enhancement have been considered by a number of authors.[6-9] Following Bourgoin and Corbett,[7] the mechanisms can be conveniently divided into two general classes:

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1. Charge state effects. The migrational barrier in general will depend upon the charge state of the defect. Under injection conditions, a non-equilibrium charge state with a lower barrier may be generated, supplying a faster diffusing path.

2. Charge state alternation effects. Here it is the change in the charge state which drives the diffusion. There are two possibilities:

a. Saddle point (Bourgoin)[10] mechanism. In this special case, the defect stable configuration in one charge state is the saddle point configuration for migration between two stable positions for the other charge state, and vice versa. This would give rise to a highly efficient and athermal mechanism, the defect making one diffusional jump for every two charge state change cycles.

b. Energy release mechanism. Here the electronic energy released upon capture of a carrier is converted to kinetic energy of the atoms associated with the defect, assisting it over the barrier. This can give rise to athermal or thermally activated motion depending upon whether the energy released exceeds or is less than the barrier. The efficiency of this mechanism depends critically on how efficiently this vibrational energy can be channeled into the appropriate diffusive mode and how long this energy is available before it is radiated away as phonons.

In GaAs and GaP, it was concluded that the enhancement was due to the energy release mechanism.[6] Unfortunately, however, none of the defects involved has been identified. In silicon we have the advantage of well identified defects. In this paper, therefore, we will explore this phenomenon for radiation-produced defects in silicon.

II. Previous Evidence in Silicon

In Figure 1, we summarize the low temperature damage process as deduced from EPR studies for p-type silicon irradiated by 1.5 MeV electrons

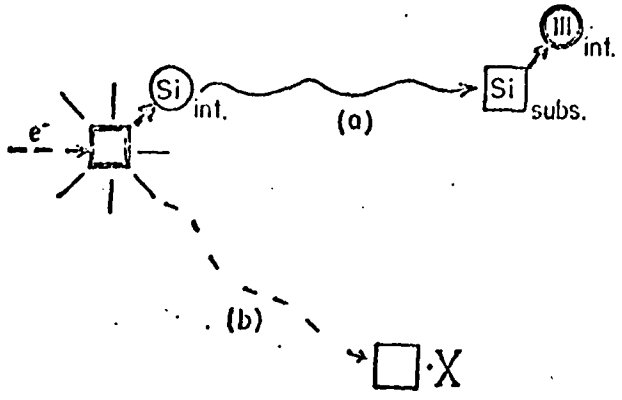

Fig. 1. Low temperature damage process in p-type silicon.
(a) Interstitial silicon migrates until trapped by a group III atom, displacing it into the interstitial site.
(b) Limited vacancy migration produces some vacancy-impurity pairs.

at 4.2-20.4K. In the primary damage event, silicon atoms are displaced in a Rutherford scattering event, producing vacancies and interstitials in equal numbers. The experimental observation, however, is that the dominant defects present after the irradiation are isolated lattice vacancies and interstitial group III atoms, in approximate 1:1 concentrations.[11-13] No isolated silicon atoms have been detected. It has been concluded, therefore, that the interstitial atom is unstable, migrating long distances during the irradiation and being trapped by a substitutional group III atom, trading places and ejecting the group III atom into the interstitial site. The mechanism for this motion is not known, but it has long been speculated[14-16] that this is a manifestation of ionization enhanced migration, a large concentration of electron-hole pairs being generated during the irradiation.

Also noted immediately after the irradiation has been a small concentration of vacancy-impurity pairs, greatly in excess of what would result simply from random damage creation in the vicinity of the impurities.[13] Since thermally activated migration of vacancies should be negligible at these temperatures, it could be concluded that the vacancy also is executing limited migration during the irradiation.

Because isolated vacancies can be produced, it is possible to study their motion directly by introducing ionization separately after the original damage producing irradiation. Work in progress on this will be described in this paper. The interstitial is not so easy because we cannot freeze it out for direct study. For hints as to its properties we will describe studies of the interstitial impurities which were formed by trapping the silicon interstitial. We will find that interstitial boron and aluminum also display ionization enhanced migration.

III. Vacancy

Deep level transient capacitance spectroscopy (DLTS) studies have detected a level at E_V + 0.13 eV in irradiated p-type silicon which arises from the lattice vacancy.[17-19] The results of annealing studies in these experiments[17] are summarized in Figure 2. Under zero bias conditions (F_V +

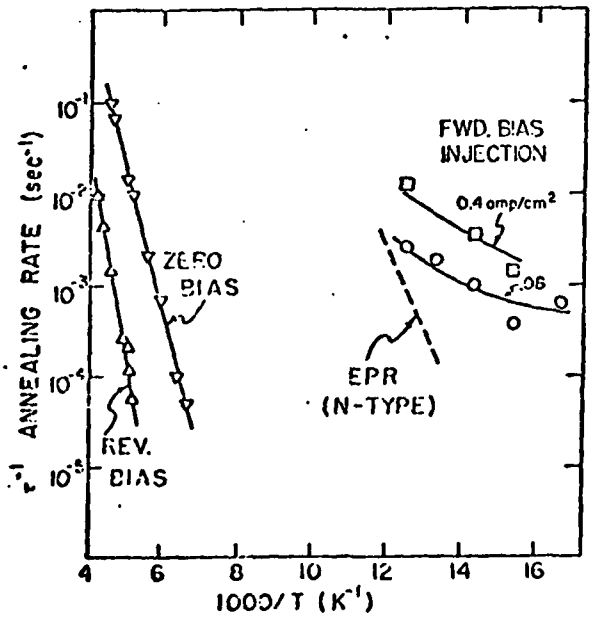

Fig. 2. Annealing kinetics for the E_V + 0.13 eV level identified with the lattice vacancy. Shown also are the kinetics for vacancy anneal in low resistivity n-type silicon from EPR studies (ref. 13).

0.13 eV level empty), the activation energy for the disappearance of this level is 0.32±.02 eV, in excellent agreement with that previously determined by EPR studies.[20] Under reverse bias (level filled with electron), the activation energy is 0.45±.04 eV. Shown also is the vacancy annealing in n-type material from EPR studies,[13] with activation energy 0.18±.02 eV. These experiments have been performed under conditions where the dominant impurity trap for the vacancy is neutral (interstitial oxygen, substituional tin) and therefore the changes in the activation energy should not be reflecting Coulombic temperature dependent capture cross sections but rather must reflect the activation energy for migration in different vacancy charge states. The charge state dependence is therefore well established and provides a possible mechanism for ionization enhanced migration. Indeed, Gregory[1] interpreted his injection enhancement results by this mechanism, the faster diffusing charge state in n-type silicon presumably being generated in the p-type material under injection conditions. In Figure 2 we show also our results for annealing of the E_V + .13 eV level under forward bias injection conditions.[21] We note that the annealing rate is essentially temperature independent and significantly exceeds that for the n-type charge state. We can conclude, therefore, that the injection enhancement reflects more than simply a charge state effect, and must involve charge alternation, presumably resulting from electron-hole pair recombination at the defect.

This has also been studied directly by EPR,[17,21] where injection is achieved by illumination from a Nd YAG 1.064μ laser at 4.2-20.4K. A typical result is shown in Fig. 3 where vacancy migration and trapping by germanium is monitored

$$V + Ge \underset{K_2}{\overset{K_1}{\rightleftarrows}} V \cdot Ge \qquad (1)$$

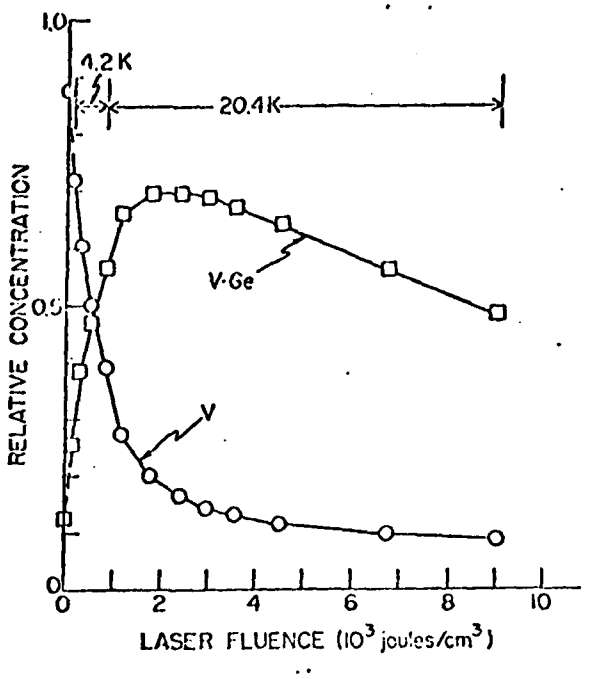

Fig. 3. Nd-YAG laser annealing of vacancies and vacancy-germanium pairs monitored by EPR in p-type silicon (Al, 3×10^{16} cm^{-3}; Ge, $5\times10^{18}cm^{-3}$) at cryogenic temperatures.

For this study, a floating zone p-type silicon sample (Al, 3×10^{16} cm^{-3}) which had been doped with 5×10^{18} cm^{-3} germanium was first irradiated at 20.4K with 2.4MeV electrons to a fluence of 2.7×10^{16} el/cm^2. The intensities of the isolated vacancy and vacancy-germanium pair EPR spectra were then monitored vs. laser illumination fluence. The vacancies are observed to convert quickly to V·Ge pairs approaching a constant ratio of ~5:1 pairs to isolated vacancies. This demonstrates that long range migration of the vacancy is occurring to produce the pairs (K_1) and also, at the same time, the reverse reaction to regenerate the vacancies from break-up of the pairs (K_2) is also being stimulated. (The break-up can also be convincingly demonstrated by a 180K anneal which converts all to V·Ge pairs, with the subsequent regeneration of vacancies by the laser illumination[17].) The slower decay of both spectra presumably reflects the trapping of vacancies at competing traps.

In these experiments, the internal temperature of the sample can be monitored directly by monitoring the spin lattice relaxation times of the

spectra. We estimate a 1K rise in temperature for a laser flux of $\sim$0.6 W cm^{-2}. Most of our studies have been performed at fluxes an order of magnitude lower and the temperature rise is therefore negligible.

Consistent with the DLTS findings of Fig. 2, we find the process athermal, the rate being essentially the same at 4.2K and 20.4K. The rate is linearly proportional to laser intensity. Normalized to a laser flux of 1W cm^{-3}, the results of Fig. 3 give

$$K_1 \sim 10^{-3}\ s^{-1} . \qquad (2)$$

The solution to the diffusion equation gives

$$K_1 = 4\pi NRD \equiv 4\pi N\nu a^3/6 \qquad (3)$$

where N is the concentration of traps (Ge), R is a capture radius (set equal to a, the nearest neighbor distance), D is the vacancy diffusion constant, and ν is the single jump frequency for the vacancy. Equations (2) and (3) therefore imply a jump frequency of $\sim$10 sec^{-1} at an excitation level of 1 W cm^{-3} (5.4 x 10^{18} photons/sec). Estimating a vacancy concentration of $4\times10^{15}cm^{-3}$, this means a vacancy makes one jump for every $\sim$150 photons absorbed in the sample. This is a fairly efficient process, even if all of these photons interacted only with the vacancies (either directly, or indirectly by electron-hole pair generation and recombination at the vacancy), which is certainly not necessarily the case.

Ionization enhanced migration has also been studied by EPR in n-type silicon.[21] Counterdoped n-type pulled silicon (P, 3 x 10^{16} cm^{-3}; B, 1 x 10^{16} cm^{-3}; O, 8 x 10^{17} cm^{-3}) was first irradiated with 1.5 MeV electrons at 20.4K, to a fluence of 1.1 x 10^{17} cm^{-2}. The migration of vacancies and trapping by oxygen was then monitored vs. laser fluence. The results are shown in Fig. 4(a). As previously observed by EPR studies of the annealing in the dark,[13] the reaction is

$$V + O_i \xrightarrow{K_1} (V\cdot O)^* \rightarrow V\cdot O , \qquad (4)$$

where an excited configuration of the vacancy-oxygen pair (V·O)* is first formed. Under laser excitation, no reverse reaction break-up of the (V·O)*

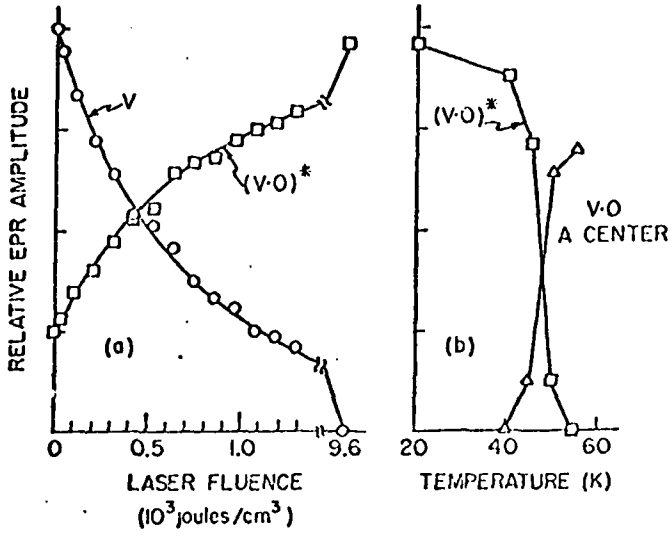

Fig. 4. (a) Nd-YAG laser annealing at 20.4K of vacancies in counterdoped n-type pulled silicon (P, $3\times10^{16}cm^{-3}$; B, $1\times10^{16}cm^{-3}$; O, $8\times10^{17}cm^{-3}$), as monitored by EPR. (b) Subsequent isochronal (15 min) anneal in the dark.

pair is observed (the conversion is complete), and no conversion to the ground state configuration V·O occurs. This is particularly remarkable because warming in the dark to only 50K is sufficient to convert completely to the V·O state, Fig. 4(b). Subsequent laser excitation does not regenerate (V·O)*. Apparently the ionization enhanced processes can be very selective!

Again, the reaction constant K_1 is found to be $\sim10^{-3}$ sec^{-1} for 1 W cm^{-3} laser excitation. With Eq. (3), an estimate of the vacancy concentration of 2×10^{15} cm^{-3}, and $N = 8.10^{17}$ cm^{-3}, we estimate one jump for every 50 photons absorbed by the sample.

The ionization enhanced migration process for the vacancy is therefore efficient and comparable in both n- and p-type material at temperatures below carrier freeze out, where these experiments were performed.

IV. Interstitial Boron

A level at E_c-0.45 eV has been observed by DLTS studies which we have identified with interstitial boron.[22] It is the dominant level produced by 1.5 MeV electron irradiation at 4.2K in counterdoped (P ∿ 3 x 10^{16} cm^{-3}, B ∿ 1 x 10^{16} cm^{-3}, O ∿ 8 x 10^{17} cm^{-3}) n-type silicon. Annealing studies on this level are presented in Fig. 5. The zero bias results (level filled)

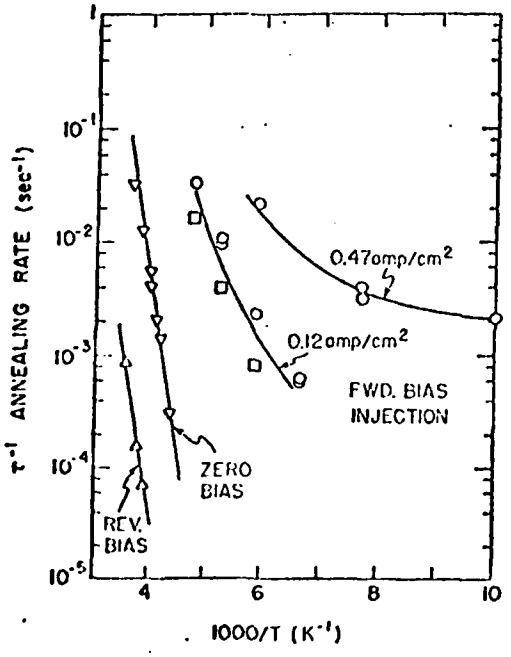

Fig. 5. Annealing kinetics of the E_c-0.45 eV level identified with interstitial boron in counterdoped n-type silicon.

match closely those observed by EPR for interstitial boron in similar counter-doped n-type material and the reverse bias results (level empty) match closely those seen in p-type material by EPR.[12] Again, therefore, there is a strong charge state effect; however, again as for the vacancy, the large enhancement observed under injection conditions, Fig. 5, reveals a recombination enhanced mechanism.

This effect was anticipated in earlier EPR results where it was demonstrated that interstitial boron could be made to jump from one distorted configuration to another by laser excitation at 20.4K while the thermal activation barrier of 0.6 eV required temperatures of ∿200K in the dark.[12] There the efficiency was estimated to be ∿ one jump per thousand electron captures.

V. Interstitial Aluminum

In DLTS studies, a level at E_V + 0.17 eV produced by electron irradiation of aluminum-doped silicon has been identified as the second donor state of interstitial aluminum.[17,23] Annealing results for this level are seen in Fig. 6. Zero or reverse bias makes only a minor difference in this case,

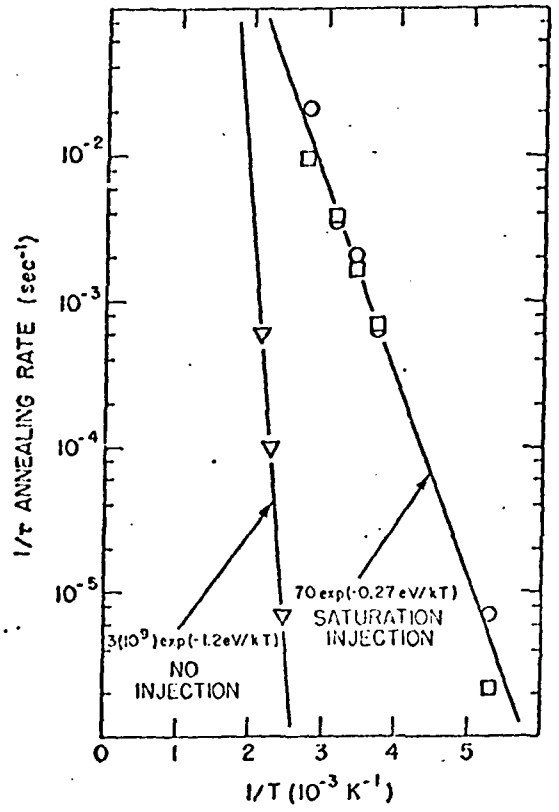

Fig. 6. Annealing kinetics of the E_V+0.17 eV level identified with interstitial aluminum.

the activation energy for anneal being 1.2 eV. The defect is therefore normally stable at room temperature, annealing at ∿200 C.

Forward bias injection of the diodes greatly enhances the annealing. The rate is observed to be proportional to the injection current density at low injection levels but saturates at ∿1 amp/cm^2 in the diodes studied (Al ∿ 10^{16}/cm^3). This is a characteristic signature of a recombination enhanced process, the low injection rate being limited by electron capture,

and saturation reflecting the majority (hole) capture as the rate limiting process. The results shown in the figure are for saturation injection conditions.

This is a dramatic effect, an increase of 10^8 having occurred at room temperature. In this case, the process is still thermally activated (0.27 eV). This represents a remarkable energy efficiency, essentially 0.9 eV of the maximum available electron-hole pair recombination energy ($E_g \sim 1.1$ eV) has been converted to assist the atom over the barrier!

A detailed study of this has recently been published.[23] By combining EPR and DLTS studies, an unambiguous identification of the annealing process as long range diffusion of the interstitial aluminum atom has been made. By detailed analysis of the DLTS studies it has also been possible to demonstrate that it cannot be recombination at the $E_V + 0.17$ eV second donor level observed in DLTS that causes the motion. Instead it must be recombination at a single donor state, tentatively located at $E_c - 0.2$ eV. It was also possible in this case to rule out the Bourgoin mechanism.

VI. Other Defects

Several other defects have been observed to display ionization enhanced annealing. The Si-G-25 center, tentatively suggested to be a silicon interstitial observed by EPR in n-type material,[13] anneals quickly at 20.4K under laser injection.[24] Other weak centers seen in low temperature irradiation in both DLTS and EPR studies, but which are not yet identified, also anneal similarly.

Particularly interesting is the recent observation by Kimerling et al.[25] that a DLTS level in n-type material at E_c-.12 eV, which they identify as arising from interstitial carbon, emerges upon injection at 77K while thermally it emerges at ~150K. We also have confirmed these results. If the

identification as interstitial carbon is correct this may supply another important clue, if we can unravel it, to the interstitial story.

VII. Discussion

We have found that ionization enhanced motion is remarkably common for radiation produced defects in silicon. For the three example we have discussed in detail here, we conclude that the mechanism is a recombination enhanced one, the motion requiring the charge state alternation associated with electron and hole capture. In the case of interstitial aluminum it has been possible to demonstrate that it must be an energy release mechanism. For the other defects, the Bourgoin mechanism cannot be ruled out at this stage.

Both the Bourgoin and energy release mechanisms imply a configurational instability associated with a change in charge state at the defect. In the case of the vacancy, this can be understood in terms of the large and different Jahn-Teller lattice relaxations that have been detected from EPR studies[13] for the vacancy charge states V^+, V^o, and V^-. Change between these charge states by carrier capture give the neighbors a "kick" as they are propelled to their new equilibrium positions providing the kinetic energy needed for the energy release mechanism. An alternate possibility is that $V^=$ has a stable saddle point configuration and the Bourgoin mechanism operates between V^- and $V^=$, as suggested by Bourgoin and Corbett.[26] Further experiments will be required to distinguish between these two mechanisms.

In the case of interstitial aluminum, we have been able to identify the $(0/+)$ transition as the charge state alternation cycle responsible for the motion. This suggests the following simple model: As a free ion, Al^{++} has a $3s^1$ configuration and Al^+, $3s^2$. Both of these ions might therefore be expected to be stable in the "normal" high symmetry tetrahedral (T_d) interstitial site. This is confirmed directly by EPR studies for the Al^{++} state.[11,27] Al^o, however, has a $3s^23p$ configuration and a Jahn-Teller

instability would be predicted, with the atom moving out of position possibly into a "bonded" interstitialcy configuration. (This tendency is confirmed for interstitial C^+ and B^o both also of s^2p configurations which are found to have low symmetry configurations directly by EPR.[12,28]) Charge alternation between the neutral and ionized state therefore would supply the necessary energy release as the atom is propelled back and forth between the two configurations. Presumably the $B_i^o \rightleftarrows B_i^+$ transition is similarly responsible for the interstitial boron migration.

This gives us a possible clue to the interstitial silicon migration mechanism mentioned at the beginning. Silicon lies next to aluminum in the periodic table and as an interstitial might also be expected to provide two donor levels. Here, however, it would be the second donor state $Si^+(3s^23p)/Si^{++}(3s^2)$ which would provide the corresponding instability. Otherwise, the process would be similar to that for interstitial aluminum but with one small but important difference: The delicate balance between the energy released E_R and the barrier E_B has switched, $E_R > E_B$, so that the process is athermal, as is apparently the case for interstitial boron.

At the same time, the efficiency must be high. This means that the defect must be an effective recombination center, and, at the same time, for every recombination cycle, the probability of a jump must be near unity in order to explain the apparent absence of detectable unannealed self interstitials after the irradiation. This makes the self interstitial a good candidate for the Bourgoin mechanism with its inherent high efficiency. On the other hand, we have previously shown that the preexponential factor for the aluminum migration also implies a near unity conversion factor.[23] What this really means is that the released energy upon carrier capture is directed efficiently into the diffusive mode for the defect. In other words, it gives it a kick in the right direction.

VIII. Acknowledgments

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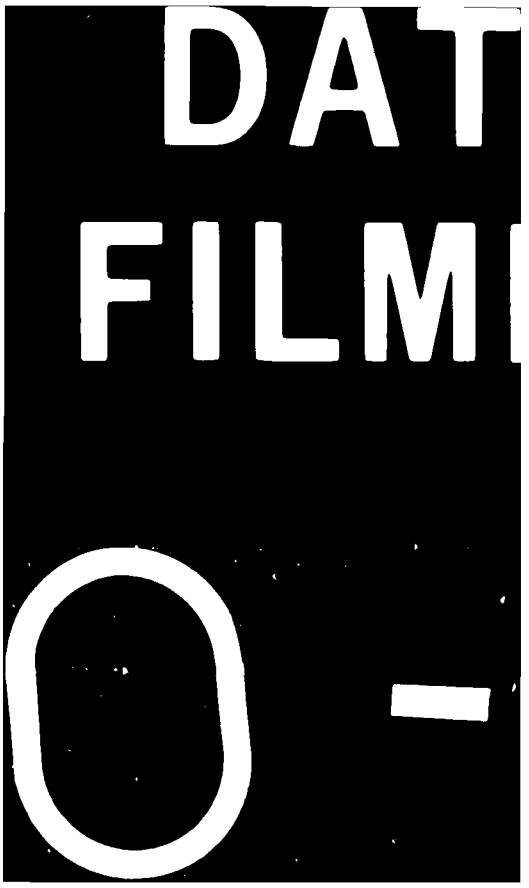
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